PNL-4013
UC-11
1-

Treatment of Biomass Gasification Wastewaters By Wet Air Oxidation

C. J. English

September 1981

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

PNL-4013

Battelle

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy $________*; Microfiche $3.00

*Pages	NTIS Selling Price
001-025	$4.00
026-050	$4.50
051-075	$5.25
076-100	$6.00
101-125	$6.50
126-150	$7.25
151-175	$8.00
176-200	$9.00
201-225	$9.25
226-250	$9.50
251-275	$10.75
276-300	$11.00

PNL-4013
UC-11

TREATMENT OF BIOMASS GASIFICATION WASTEWATERS BY WET AIR OXIDATION

C.J. English

September 1981

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO-1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

Use of brand or trade names in this report does not constitute endorsement of equipment or products by the U.S. Department of Energy or Pacific Northwest Laboratory.

ACKNOWLEDGMENTS

The author gratefully acknowledges the efforts of Terry Lambright and Pete Swift, of the Materials Department, who prepared and operated the autoclave used in these experiments. I also wish to thank Scott Eliason and Marie Laegreid, of the Water and Land Resources Department, and Wayne Wilcox, of the Chemical Technology Department, who performed the chemical analyses. I also appreciate the efforts of Nancy Painter, who typed the manuscript.

I also wish to acknowledge Dr. Steven Beck, of Texas Tech University, who furnished the wastewater samples, and Mr. Ray Costello, of the U.S. Department of Energy, who was project officer for this work.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

Production of synthetic natural gas from gasification of biomass results in the generation of a high-strength wastewater that is difficult to treat by conventional means. This study investigated the use of wet air oxidation (WAO) as a treatment method for these wastewaters. A literature review was conducted to identify the suitability of WAO for the treatment of high-strength industrial wastewaters and to determine typical operating conditions for such treatment. Data presented in the literature showed that WAO should be suitable for treatment of biomass gasification wastewaters (BGW), and a laboratory treatability study was designed. BGW, having an initial chemical oxygen demand (COD) of 30,800 mg/l and initial color of 183,000 APHA units, was treated in a laboratory autoclave for 20, 40, 60, 120, and 180 min at temperatures and pressures of 150°C, 5.1 MPa (750 psi); 200°C, 6.9 MPa (1000 psi); 250°C, 10.3 MPa (1500 psi); and 300°C, 13.8 MPa (2000 psi). Maximum COD removals of 0% for the 150°C, 5.2 MPa (750 psi) runs; 40% for the 200°C, 6.9 MPa (1000 psi) runs, 55% for the 250°C, 10.3 MPa (1500 psi) runs; and 85% for the 300°C, 13.8 MPa (2000 psi) runs were measured. Maximum color removals for these respective runs were 56%, 82%, 97%, and 99%. Initial removal rates of COD and color were observed to increase with reaction temperature. The experimental results suggest that oxidation of BGW organics by WAO occurs in a stepwise fashion with large organic molecules first being hydrolyzed and then partially oxidized to low molecular weight intermediates. Complete oxidation of these intermediates is more difficult and most easily accomplished at high reaction temperatures. The best application of WAO to treatment of BGW appears to be as a pretreatment to biological treatment and it is recommended that this application be investigated.

CONCLUSIONS

Treatment of BGW by WAO can be highly effective for removing both COD and color.

Removal of COD and color is highly dependent upon reaction temperatures and pressures. Both amount removed and rate of removal increase with temperature and pressure.

The degradation of organics in BGW occurs in stepwise fashion with large molecular weight organics first hydrolyzed, then partially oxidized to low molecular weight intermediates. Complete oxidation of these intermediates occurs only a high temperatures (250 to 300°C).

WAO may be very promising as a pretreatment for biological treatment.

RECOMMENDATIONS

WAO should be investigated as a pretreatment to biological treatment. Specifically, the following should be studied:

- the reduction of wastewater toxicity by WAO, as measured by common bioassay techniques;
- the destruction of specific toxic or inhibitory organics in BGW by WAO;
- the treatability of WAO effluents by various biological treatment methods, including land application; and
- the effect of short WAO reaction times (0-20 min) on all of the above.

These results could then be used to define an optimum WAO/biological treatment system which could then be studied at bench or pilot scale.

INTRODUCTION

Thermochemical conversion of biomass (animal manure, wood chips, straw, etc.) is being developed as a source of synthetic natural gas. In the process of gasification, water and some organic chemicals condense to form a wastewater too strong for treatment by conventional means (e.g., activated sludge). Several laboratory scale methods for treating these wastewaters have been previously investigated at the U.S. Department of Energy's Pacific Northwest Laboratory (PNL) by Maxham and Wakamiya (1980a, 1980b) and Maxham and Bell (1980). These methods consisted of several types of biological treatment, both aerobic and anaerobic, and solvent extraction. This study was undertaken to initially investigate the suitability of the WAO process for treatment of BGW. Wastewater for this study was obtained from the Synthesis Gas From Manure (SGFM) gasifier at Texas Tech University in Lubbock, Texas. Characteristics of this wastewater are given in Table 1.

TABLE 1. Characteristics of Biomass Gasification Wastewater

COD	30,800 mg/l
TOC	12,700 mg/l
Total Dissolved Solids	18,500 mg/l
Total Suspended Solids	4,100 mg/l
Color	183,000 APHA Units
Total Ammoniacal Nitrogen	3,300 mg/l
Total Kjeldahl Nitrogen	5,700 mg/l
pH	6.4

WAO is a thermal treatment method that is particularly well suited for treatment of high-strength organic wastewaters. During the process, wastewater is brought to high temperature (150 to 300°C) and pressure (3 to 20 MPa) in the presence of oxygen. Under these conditions, most organic contaminants in the wastewater will undergo partial or complete oxidation.

The general approach of this study was to review current technical literature related to the application of WAO to treatment of industrial wastes and to conduct a limited laboratory scale treatability study of BGW using WAO. Specific objectives of the study were:

- to determine the effectiveness of WAO in removing organic contaminants from BGW (as measured by removal of COD);
- to determine the effect of gross operating variables (temperature, pressure, and reaction time) on the degree of COD removal;
- to gain a general understanding of the mechanisms involved in COD removal by WAO; and
- to identify potential applications for WAO in the treatment of BGW, either alone or in combination with other treatment methods.

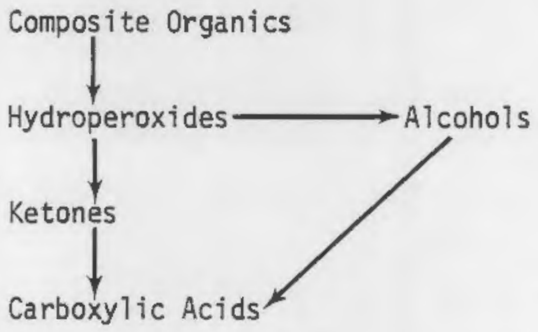
LITERATURE REVIEW

DEGRADATION OF ORGANICS DURING WET AIR OXIDATION

The degradation of wastewater organics during WAO was described by Pujol, Talayrach, and Besombes-Vailhe' (1980); Takeichiro, Hashimoto, and Sioya (1970); Teletzke (1964); and Wilhelmi and Ely (1977). Degradation occurs in a stepwise fashion involving three steps. These are thermal decomposition, partial oxidation, and complete oxidation. Organic contaminants may undergo any or all of these degradation processes depending on the composition of organics and the characteristics of the treatment process.

Thermal decomposition involves the dissolution and hydrolysis of large organic molecules without oxidation. Thermal decomposition of activated sludge during WAO was studied by Takeichiro, Hashimoto, and Sioya (1970). They reported that decomposition rates were dependent upon temperature and that thermal decomposition of activated sludge was characterized by a decrease in particulate COD, an increase in soluble COD, and no change in total COD. Thermal decomposition usually precedes other degradation processes with large molecules, though this is not absolutely necessary.

Partial oxidation involves the oxidation of large high molecular weight organic molecules to lower molecular weight intermediates such as aldehydes, alcohols, and fatty acids (Wilhelmi and Ely 1977). Pujol, Talayrach, and Besombes-Vailhe' (1980) described the order of reaction as:



Carboxylic acids are the most stable intermediates formed, and are very resistant to further degradation by WAO. Organic nitrogen compounds are partially oxidized to ammonia and low molecular weight organic intermediates (Teletzke 1964).

Complete oxidation involves oxidation of organic intermediates to carbon dioxide and water. No evidence could be found to suggest that ammonia is oxidized under typical WAO operating characteristics.

Wilhelmi and Knopp (1970) described the general relationship between COD, biochemical oxygen demand (BOD), and volatile acid concentrations during the degradation of organics by WAO. Initially, COD will decrease while BOD and volatile acids increase. This results from the decomposition and partial oxidation of large nonbiodegradable organic molecules to smaller, more easily biodegradable molecules. The COD then continues to decline while BOD reaches a maximum value and volatile acids increase. This is due to partial oxidation of organic constituents and formation of volatile acid intermediates. Finally, the COD, BOD, and volatile acids will all decline as volatile acid intermediates are completely oxidized to carbon dioxide and water.

The relative predominance of the above degradation processes depends on several factors such as the partial pressure of oxygen, the reaction temperature, and the length of reaction. If oxygen is not present, oxidation is impossible and only thermal decomposition will occur. Day, Hudgins, and Silveston (1973) reported that WAO reaction rates were first order with respect to oxygen partial pressure. Pujol, Talayrach, and Besombes-Vailhe' (1980) investigated the effect on oxidation rate of increasing oxygen partial pressure while holding temperature constant. Generally, higher partial pressures resulted in more rapid oxidation of organics. The magnitude of this effect depended on reaction temperature. At the low temperatures studied (220°C), there was a substantial difference in oxidation rates between the various pressures. At the high temperature studied (295°C), there was only a slight difference.

Generally, increasing temperature increases reaction rates. The effect of temperature on the oxidation of a specific compound depends on the activation energy for the oxidation of that compound. Teletzke (1964) treated several classes of compounds for 1 hr at various temperatures. In general, he reported low degrees of oxidation between 100 and 150°C, a large increase in degree of oxidation between 150 and 225°C, and a small but study increase in degree of oxidation between 225 and 330°C. Teletzke et al., (1967) investigated the degradation of different sludge components during WAO at various temperatures. Starch was the most easily degraded component at all temperatures. At temperatures below 220°C, lipids were the most resistant; however, above 200°C lipids were degraded almost as readily as starch. Proteins and crude fibers were degraded intermediate between starch and lipids below 200°C and less easily than starch and lipids above 200°C. At low temperatures, the primary degradation mechanism identified was hydrolysis of large macro-molecules to constituent components. At high temperatures the less stable of these constituents were oxidized.

Plots of degree of oxidation vs time were presented by Day, Hudgins, and Silveston (1973); Ottengraf and Lotens (1978); Teletzke (1964); and Zimmerman (1958). In general, these results suggest that oxidation of organic material by WAO follows first order reaction kinetics.

APPLICATION OF WET AIR OXIDATION TO WASTEWATERS

Commercially available WAO equipment has been most widely used for the stabilization of municipal sewage sludge. However, the process has also been investigated for and applied to a number of industrial and toxic wastewaters. Wilhelmi and Ely (1977) report results of development programs for three toxic industrial waste streams. WAO of an acrylonitrile wastewater having a COD of 42,000 mg/l and cyanide concentration of 270 mg/l resulted in 97% reduction of COD and over 99% reduction of cyanide. This effluent was highly treatable biologically and final effluent from combined WAO/biological treatment had a COD of 325 mg/l (>99% removal), BOD_5 of 10 mg/l, and a cyanide concentration of 1 mg/l. WAO was also investigated for a complex organic chemical manufacturing wastewater which could not be treated biologically. WAO reduced the COD from 55,000 mg/l to 14,000 mg/l (75% removal), and the BOD_5 from 23,000 mg/l to 8,400 mg/l (63% removal). The WAO effluent could then be treated biologically to achieve an effluent COD of 300 mg/l (>99% removal overall), and BOD_5 of 30 mg/l (99.9% removal overall). WAO was also investigated for treatment of wastewaters from pesticide manufacture. Average results show that WAO increased the BOD/COD ratio of the wastewater from 0.27 to 0.85. This indicates a great increase in the biological treatability and possibly a reduction in the toxicity of the wastewater.

Pradt (1972) reported results of WAO treatment of a phenol-containing chemical plant wastewater. The average COD was removed from 76,300 mg/l to 37,400 mg/l (51% reduction), and phenols were reduced from 3,300 mg/l to 8 mg/l (99.8% reduction). Pruden and Le (1976) also investigated WAO treatment of phenol wastes and reported 98% removal of phenol, of which 91% was converted completely to CO_2.

Wilhelmi and Knopp (1979) reported results of laboratory testing of WAO treatment of municipal sewage sludge highly contaminated with the toxic chemicals hexachlorocyclopentadiene (HCCP) and octachlorocyclopentadiene (OCCP). Low temperature and pressure WAO resulted in over 90% removal of these chemicals from the sludge.

Randall and Knopp (1980) investigated the destruction of ten organic priority pollutants in wastewater using WAO. With treatment at 275°C, levels of most of the priority pollutants were reduced over 99% and all had been reduced at least 82%. With treatment at 320°C, levels of all ten priority pollutants were reduced 99.9%. Toxicity of the treated and untreated wastewaters was assessed using Daphnia magna bioassays. For both the 275 and 320°C treatments, the toxicity of the treated wastewater had been reduced by at least one order of magnitude and, in most cases, by two orders of magnitude.

WAO has also been applied to treatment of industrial wastewaters containing inorganic contaminants. Wilhelmi and Knopp (1979) reported results of WAO treatment of coke oven gas scrubbing wastewaters containing high concentrations of cyanide, thiocyanate, and thiosulfate. Treatment resulted in essentially complete oxidation of all waste constituents and allowed recovery of ammonium sulfate and sulfuric acid.

DEVELOPMENT OF EXPERIMENTAL APPROACH

The overall objectives of the laboratory study were to determine the effectiveness of the WAO process for treating BGW and to gain a general understanding of the mechanisms involved in treatment. Development of an experimental approach to meet these objectives involved the following steps:

- select and develop apparatus for laboratory scale WAO treatment of BGW;
- determine operating conditions for laboratory treatment experiments; and
- select analytical methods and procedures to obtain the necessary data to evaluate WAO treatment.

SELECTION OF LABORATORY SCALE TREATMENT APPARATUS

Literature describing previous laboratory scale WAO studies was reviewed to identify the experimental apparatus used. Day, Hudgins, and Silveston (1973) oxidized propionic acid solutions in a stirred 1 l autoclave which was plumbed to allow liquid samples to be withdrawn during experimental runs. They experimented with several stirrer speeds and found that 450 rpm provided sufficient agitation for oxygen transfer into the solution. Marshall and Gillespie (1975) also employed a stirred autoclave for WAO experiments, but operated the stirrer at 1750 rpm. This higher speed was probably necessary because they were treating sewage sludge, which is much more viscous than wastewater. The autoclave they employed did not allow samples to be withdrawn without disassembly. Additionally, the vessel was equipped with an internal cooling coil to help control the reaction. Pruden and Le (1976) made use of a continuous flow 1 l WAO reactor to treat wastewater samples. Pressurized liquid and gas were injected into the reactor, which was not otherwise agitated. Ottengraf and Lotens (1978) treated sewage sludge in a 600 ml shaker autoclave which was equipped for injection and withdrawal of both gas and liquid samples. An agitation rate of 143 min^{-1} was used. Pujol, Talayrach, and Besombes-Vailhe' (1980) also used a shaker autoclave in experiments involving treatment of pulp mill soda black liquor. They evaluated degree of oxidation vs agitation rate at constant temperature and determined that 500 min^{-1} provided adequate agitation for the 1 l reactor. Finally, Takeichiro, Hashimoto, and Sioya (1970) made use of 16 ml batch reactors which were not agitated. Agitation for oxygen transfer was unnecessary because their study was concerned with thermal decomposition rather than WAO.

From the review of prior WAO laboratory work, we decided that either stirred or shaker autoclaves would be suitable for laboratory scale WAO experiments. Existing equipment at PNL included several 3.78 l (1 gal) autoclaves constructed of Hastelloy C and equipped with magnetically coupled stirrers. Based upon a chemical analysis of BGW, we determined that the wastewater would not cause corrosion problems with the Hastelloy C material. One of these autoclaves was equipped for the experiments by installing a thermocouple to measure the temperature of the wastewater and a Hastelloy C cooling coil for controlling the temperature of the wastewater and quenching the reaction. A schematic of the experimental apparatus is shown in Figure 1.

SELECTION OF OPERATING CONDITIONS

Table 2 summarizes the operating conditions selected for the WAO experiments. Temperatures were chosen from a range of values reported for actual WAO treatment and similar experimental studies (Day, Hudgins, and Silveston 1973; Flynn 1979; Ottengraf and Lotens 1978; Pruden and Le 1976; and Wilhelmi and Ely 1977). The pressures associated with each temperature were selected based on considerations of performance and safety. Pressure affects performance by determining the amount of sample evaporation that will occur. Unless the system operating pressure is much higher than the saturation pressure of water at the operating temperature, the low partial pressure of water in the atmosphere above the wastewater will create a large driving force for evaporation. At high reaction temperatures (high vapor pressures) it is easily possible to completely evaporate the wastewater and stop the reaction if the reaction pressure is too low. Excessive pressure should be avoided, however, because of increased safety hazards. For the apparatus used in these experiments, 13.8 MPa (2000 psi) was the maximum pressure suggested for use. Reaction times were selected to span the range of times encountered in WAO applications.

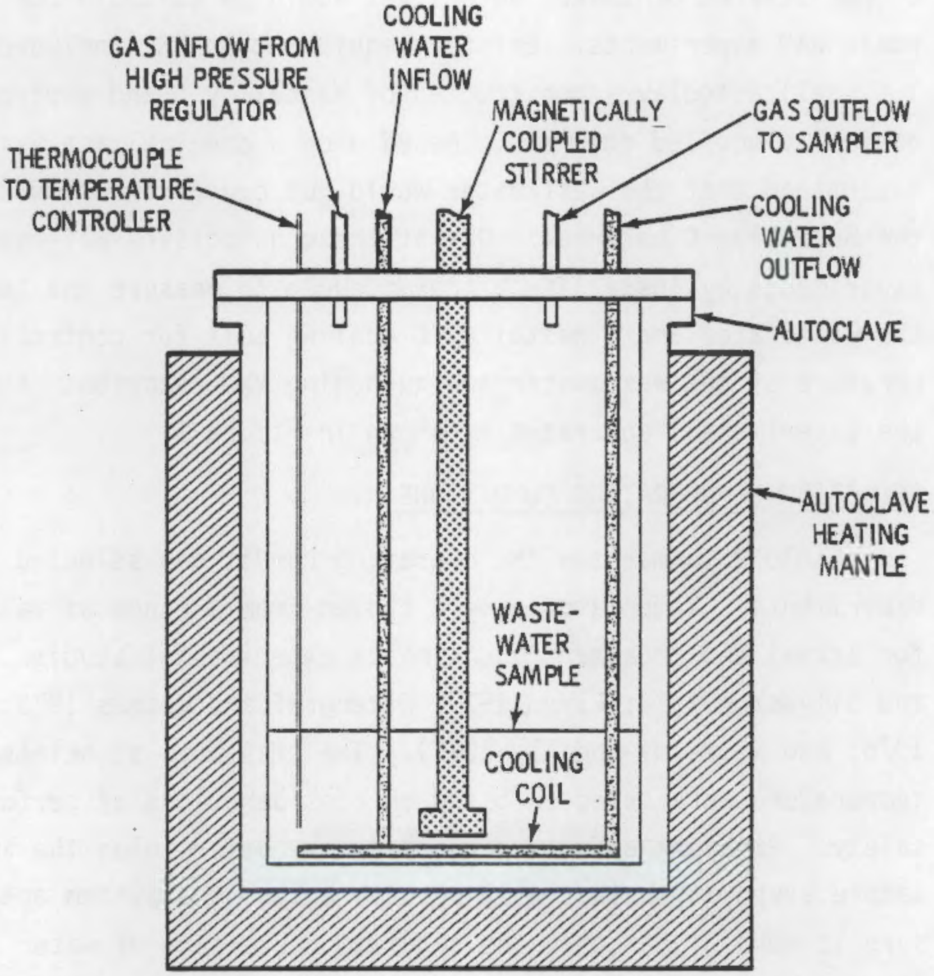


FIGURE 1. Laboratory Scale Wet Air Oxidation Apparatus

TABLE 2. Experimental Operating Conditions

Run No.	Temperature (°C)	Pressure, MPa (psi)	Reaction Time, min	Sample Vol, ml
1	150	5.2 (750)	20	690
2	150	5.2 (750)	40	690
3	150	5.2 (750)	60	690
4	150	5.2 (750)	120	690
5	150	5.2 (750)	180	690
6	200	6.9 (1000)	20	780
7	200	6.9 (1000)	40	780
8	200	6.9 (1000)	60	780
9	200	6.9 (1000)	120	780
10	200	6.9 (1000)	180	780
11	250	10.3 (1500)	20	980
12	250	10.3 (1500)	40	980
13	250	10.3 (1500)	60	980
14	250	10.3 (1500)	120	980
15	250	10.3 (1500)	180	980
16	300	13.8 (2000)	20	1130
17	300	13.8 (2000)	40	1130
18	300	13.8 (2000)	60	1130
19	300	13.8 (2000)	120	1130
20	300	13.8 (2000)	180	1130

The sample volumes were calculated from the COD of the wastewater (amount of oxygen required) and the density of air at the operating temperature and pressure (amount of oxygen available). The volumes given in Table 2 are adequate to supply 20% excess oxygen over the COD. Larger sample volumes are possible at higher temperatures and pressures since the density of oxygen in the gas phase increases (i.e., more oxygen is available per vol of air). Flynn (1979) recommended 2 to 10% excess oxygen for full-scale WAO applications. A more conservative value of 20% was chosen to allow for possible errors in COD determinations caused by the presence of large concentrations of volatile aliphatic compounds (APHA 1980). After sample volumes had been calculated from oxygen requirements, they were checked to ensure that complete sample evaporation would not occur during the experiments. The percent sample evaporation for the various samples is given in Table 3.

TABLE 3. Evaporative Loss of Samples

Run No.	Temperature (°C)	Pressure (MPa)	Percent of Sample Vol Evaporated
1- 5	150	5.2	1
6-10	200	6.9	3
11-15	250	10.3	7
16-20	300	13.8	18

The stirrer speed used for all runs was 1000 rpm. This falls within the range of 450 rpm used by Day, Hudgins, and Silveston (1973) for oxidizing aqueous acid solutions and 1750 rpm used by Gillespie (1975) for oxidizing sewage sludges. Preliminary test runs with glucose solutions using stirrer speeds of 500 rpm and 1000 rpm were conducted. No difference was seen between the degree of oxidation obtained with the two speeds. The higher stirrer speed was chosen to ensure that adequate oxygen transfer occurred.

SELECTION OF REQUIRED ANALYSES

Along with performing routine analyses to measure COD removal during treatment, analyses were needed that would give a general indication of the reaction mechanism taking place. That is, we were interested in knowing if partial or complete oxidation was occurring. Detailed analyses, such as quantitative analysis for reaction intermediates, were beyond the scope of this study. Instead, color was selected as a qualitative indicator of degree of oxidation. Color is associated mainly with long-chain aliphatic and aromatic compounds and not with short-chain aliphatics such as oxidation intermediates. A large decrease in color, accompanied by a small decrease in COD, would, therefore, indicate partial oxidation. While quantitative relationships between degree of color removal and degree of oxidation are not possible, the method should give a general indication of what is occurring during reaction.

EXPERIMENTAL PROCEDURE

Wastewater samples were transferred to the open autoclave using a graduated cylinder. The autoclave was then assembled and sealed. Bottled, compressed air was used to bring the autoclave to operating pressure. The autoclave heater was then turned on and the vessel brought to operating temperature. When the operating temperature was reached, the stirrer was turned on and the sample agitated for the period of reaction time. At the end of the reaction time, the autoclave heat and stirrer were turned off and cold water was run through the cooling coil to quench the reaction. The cooling coil was used to keep the sample cool (approximately 25°C) until the autoclave was cool enough to disassemble. At that time, the pressure was relieved and a sample of the off-gas collected in a 500 ml glass bomb. After the pressure was reduced to atmospheric, the autoclave was disassembled. The wastewater was then transferred from the autoclave to labeled polyethylene bottles using a pipette. Bottles were sealed and refrigerated at 4°C until analysis. Following each run, the autoclave was cleaned and rinsed using distilled water.

Treated and untreated wastewater samples were analyzed for COD using the procedure of Standard Methods (APHA 1980) and for platinum-cobalt color using the EPA spectrophotometric procedure (EPA 1976). The off-gas was analyzed for oxygen using gas chromatography.

RESULTS AND DISCUSSION

Figure 2 shows the COD removal vs time obtained at different reaction temperatures and pressures. These results show that the WAO process can be very effective in removing COD, with a maximum of 85% removal obtained during the most severe treatment conditions. Oxygen was present in the off-gas from all runs, indicating that COD removal was not oxygen limited.

The COD removals obtained were much higher than expected. Data presented by Kao (1980) show that 63% of the COD of a SGFM wastewater was due to acetic acid and 21% to propionic acid. These low molecular weight acids are reported to be quite resistant to oxidation by the WAO process. Day, Hudgins, and Silveston (1973) found that WAO of acetic acid was too slow for measurement under experimental conditions. One possible explanation for the high removals is that the reaction was catalyzed by some component of the wastewater.

The results also show that the degree of oxidation is very dependent on operating temperature. No COD removal was obtained at any of the low temperature runs. Previous studies showed that a greater degree of oxidation is obtained at higher temperatures (Ottengraf and Lotens 1978; Pradt 1972; Pujol, Talayrach, and Besombes-Vailhe' 1980; Teletzke 1964; and Zimmerman 1958). Our results are in agreement with this.

The effect of reaction time on COD removal appears to be strongly dependent on temperature. For the 200°C, 6.9 MPa (1000 psi) runs, the amount of COD removed increases slowly with time and appears to be still increasing at the end of 3 hrs. With the 300°C, 13.8 MPa (2000 psi) run, however, essentially all of the COD removal is accomplished within the first 20 mins. The reaction rate appears to increase with temperature, which was what we expected.

Originally we had expected COD removal rates to be first order with respect to COD concentration. The concentration of COD with time would then have been an exponential curve of the form

$$C = C_0 e^{-kt} \tag{1}$$

where C is the concentration of COD at time t, C_0 is the original concentration of COD, and k is the reaction rate constant. We expected k to vary with temperature, but to remain constant for all runs at a given temperature.

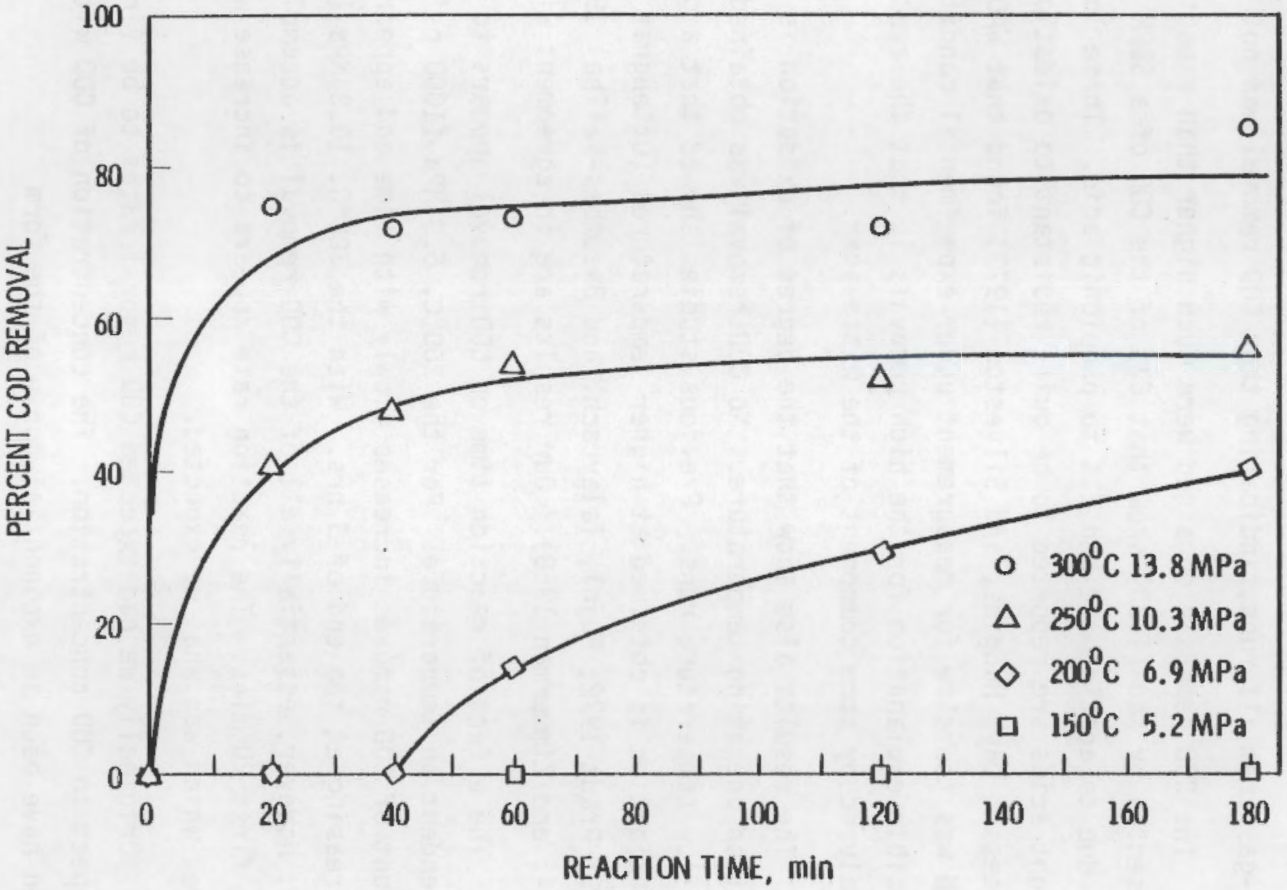


FIGURE 2. COD Removal vs Reaction Time

Linear regressions were performed to fit the experimental data to an exponential curve. A high degree of correlation was obtained with the results from the 200°C, 6.9 MPa (1000 psi) run ($r^2 = 0.96$), but poor correlation was obtained with the results from the two higher temperature runs ($r^2 = 0.50$ for both). This would suggest that first order kinetics were appropriate for the 200°C, 6.9 MPa (1000 psi) runs, but not for the runs at higher temperatures.

One possible explanation for this is that the reaction rate constant, k in Equation 1, is not constant with time. This might be explained by the work of Day, Hudgins, and Silveston (1973) who showed that the reaction rate for WAO of propionic acid was proportional to $e^{-E/RT}$, where E is the activation energy of oxidation, R is the universal gas constant, and T is the absolute temperature. If the oxidation occurs in stepwise fashion, the activation energies for the components being oxidized will increase with time since the more stable reaction intermediates have higher activation energies. Therefore, the increasing activation energies would cause the reaction constant to decrease with time. This may explain why the results of runs at the two highest temperatures fit an exponential curve so poorly. This would suggest that complete oxidation of reaction intermediates was occurring during the longer runs at the high temperatures. Conversely, the fact that the results of the 200°C, 6.9 MPa (1000 psi) runs fit an exponential curve suggests that only partial oxidation was occurring and that high activation energy intermediates were not being oxidized.

Color removal vs time for the various reaction temperatures and pressures is shown in Figure 3. Color removal displays the same trends as COD removal as far as the effects of operating conditions, which was expected. For each temperature and pressure, more color removal than COD removal was obtained for a given reaction time, particularly at the low temperatures. Care must be used in interpreting these results since the quantitative relationship between COD removal and color removal is not known. In general, however, these results indicate that stepwise degradation is occurring. For example, greater than 50% color removal was obtained with the low temperature runs while no COD removal was achieved. This would indicate that hydrolysis of large, highly colored organics was occurring without any oxidation. At the highest temperature

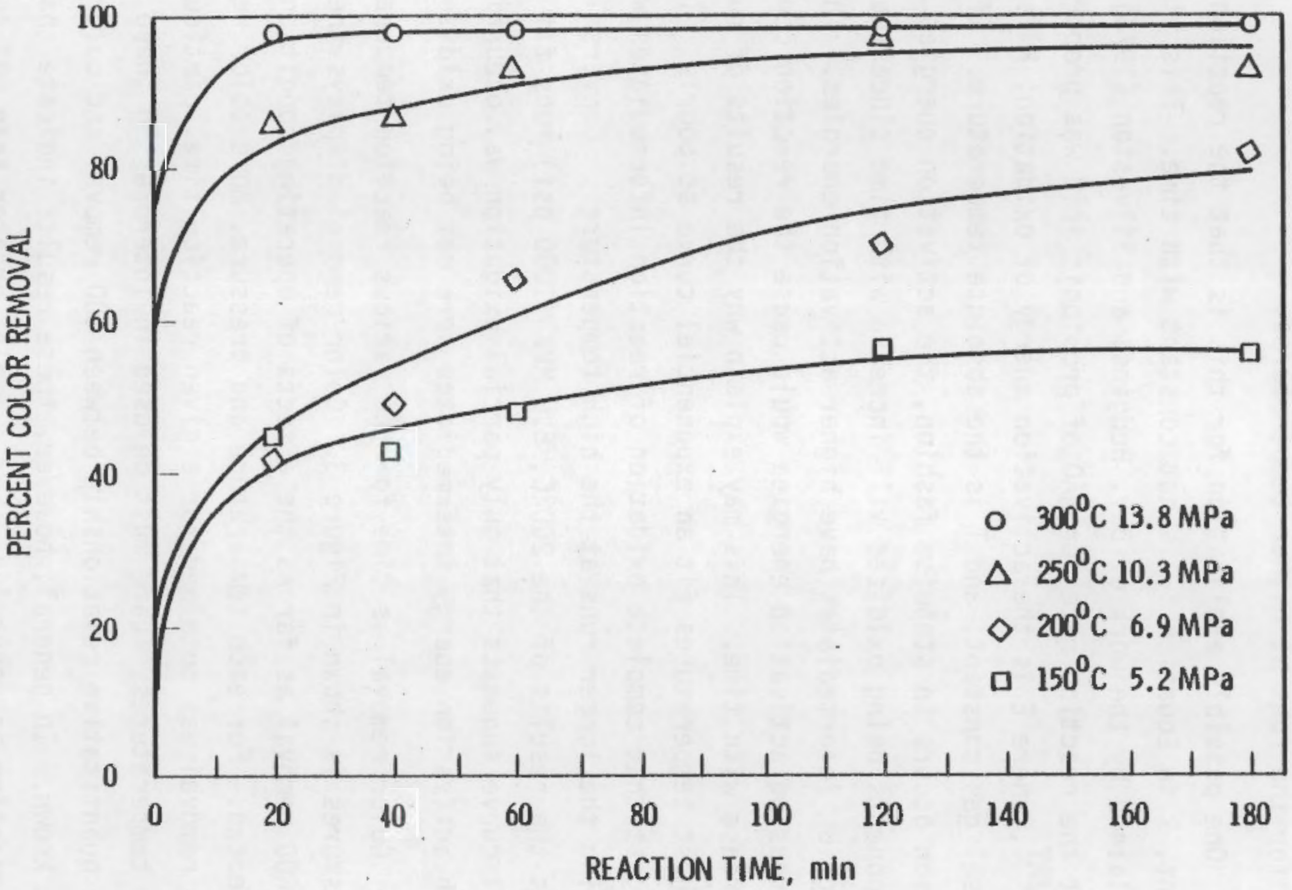


FIGURE 3. Color Removal vs Reaction Time

runs, 98% removal of color was obtained by the first sampling time (20 mins). This too would suggest that rapid degradation and partial oxidation of large organic molecules occurs before oxidation.

The results obtained suggest that the best application of WAO is probably as a pretreatment to be followed by biological treatment. Data presented by Kao (1980) show that the COD of BGW is due mainly to low molecular weight compounds (acetic acid, propionic acid, methanol, acetone, ethanol, and formic acid). As such, these wastewaters should be highly treatable by biological methods, particularly anaerobic systems. Biological treatment of BGW was studied by Maxham and Wakamiya (1980a, 1980b) and Maxham and Bell (1980). They reported difficulties in acclimating anaerobic microorganisms to full-strength BGW due to the presence of toxic and growth inhibitory organic substances. By employing pretreatment with WAO, it should be easy to partially degrade these organics into readily biodegradable intermediates. The effluent from WAO pretreatment should be highly treatable using biological means.

It was not possible with the present study to estimate the cost of treatment by WAO. WAO is a very capital intensive treatment method and most of the cost of treatment is associated with amortization of capital equipment (Wilhelmi and Knopp 1979). As such, the treatment costs would be highly dependent on the reaction times, temperatures, and pressures required. The results obtained by this study are inadequate to define operating conditions for full-scale application.

REFERENCES

APHA. 1980. Standard Methods for the Examination of Water and Wastewater. APHA, Washington, DC.

Day, D. C., R. R. Hudgins and P. L. Silveston. 1973. "Oxidation of Propionic Acid Solutions." Canadian Journal of Chemical Engineering, Vol. 51, pp. 733-740.

Environmental Protection Agency. 1976. Manual of Methods for the Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency, Cincinnati, OH.

Flynn, B. L. 1979. "Wet Air Oxidation of Waste Streams." Chemical Engineering Progress, Vol. 75, pp. 66-69.

Koa, C. 1980. Extraction of Wastewater from Biomass Gasification. M.S. Thesis, Texas Tech University, Lubbock, TX.

Marshall, D. W. and W. J. Gillespie. 1975. "Comparative Study of Thermal Techniques for Secondary Sludge Conditioning." Proceedings 29th Industrial Waste Conference, Purdue University Engineering Extension Service, Lafayette, IN.

Maxham, J. V. and N. E. Bell. 1980. Treatment of Biomass Gasification Wastewater. Presented at the 11th Biomass Thermochemical Conversion Contractors Meeting, September 23-24, Richland, WA.

Maxham, J. V. and W. Wakamiya. 1980a. "Treatability of Biomass Gasification Wastewater." Presented at the 10th Biomass Thermochemical Conversion Contractors Meeting, February 12-13, Berkeley, CA.

Maxham, J. V. and W. Wakamiya. 1980b. "Innovative Biological Wastewater Treatment Technologies Applied to the Treatment of Biomass Gasification Wastewater." Presented at the 35th Purdue Industrial Waste Conference, May 13-15, West Lafayette, IN.

Ottengraf, S. P. P. and J. P. Lotens. 1978. "Heat Treatment and Low Pressure Oxidation of Aqueous Sewage Sludge." Water Research, Vol. 12, pp. 171-178.

Pradt, L. A. 1972. "Developments in Wet Air Oxidation." Chemical Engineering Progress, Vol. 68, pp. 72-77.

Pruden, B. B. and H. Le. 1976. "Wet Air Oxidation of Soluble Components in Waste Water." Canadian Journal of Chemical Engineering, Vol. 54, pp. 319-325.

Pujol, C., B. Talayrach and J. Besombes-Vailhe'. 1980. "Modelisation De La Cinetique D' Oxydation En Phase Liquide De Liqueur Noire De Papeterie Par L' Oxygene De L' Air." Water Research, Vol. 14, pp. 1055-1059.

Randall, T. L. and P. V. Knopp. 1980. "Detoxification of Specific Organic Substances by Wet Oxidation." Journal of Water Pollution Control Federation, Vol. 52, pp. 2117-2130.

Takeichiro, T., I. Hashimoto and S. Sioya. 1970. "Model Identification of Wet-Air Oxidation Process Thermal Decomposition." Water Research, Vol. 4, pp. 33-59.

Teletzke, G. H. 1964. "Wet Air Oxidation." Chemical Engineering Progress, Vol. 60, pp. 33-38.

Wilhelmi, A. R. and R. B. Ely. 1977. "The Treatment of Toxic Industrial Wastewaters by a Two Step Process." Proceedings of the 30th Industrial Waste Conference, Purdue University. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, pp. 288-295.

Wilhelmi, A. R. and P. V. Knopp. 1979. "Wet Air Oxidation -- An Alternative to Incineration." Chemical Engineering Progress, Vol. 75, pp. 46-52.

Zimmerman, F. J. 1958. "New Waste Disposal Process." Chemical Engineering, Vol. 67, pp. 117-120.

DISTRIBUTION

No. of
Copies

OFFSITE

A. A. Churm
DOE Patent Division
9800 South Cass Avenue
Argonne, IL 60439

Ray Costello
Biomass Energy Systems Division
U.S. Department of Energy
600 E Street, N. W.
Mail Stop 404
Washington, DC 20545

27 DOE Technical Information Center

J. V. Maxham
Institute of Paper Chemistry
Appleton, WI 54911

ONSITE

Richland Operations Office

H. E. Ransom

21 Pacific Northwest Laboratory

D. B. Cearlock
G. W. Dawson
R. L. Dillon
C. J. English (10)
A. F. Gasperino
Publishing Coordination (2)
Technical Information (5)